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A review on supercritical fluids (SCF) technology in sustainable biodiesel production: Potential and challenges

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ABSTRACT

In this review, the potential of supercritical fluids (SCF) as a sustainable route for biodiesel production was discussed and compared with conventional catalytic reactions. Although the advantages of catalyst-free SCF process are apparent, there are concerns regarding the huge energy required to conduct supercritical reaction at elevated temperature and pressure. Hence, there are challenges facing SCF process which need to be addressed before it could be a sustainable technology in the future. Therefore, in this article, the challenges were elaborated thoroughly and subsequently a few constructive recommendations were proposed which could improve the process and overcome these limitations. Consequently, SCF technology will become a sustainable technology for biodiesel production and ensuring energy security in the future.

Contents

1. Introduction

The demand for fossil fuels such as petroleum and natural gas has been escalating for the past few decades owing to rapid development and urbanization that occur throughout the world [1]. In addition, the limited supply of these fossil fuels in the world market has induced the price to increase tremendously in recent years. Apart from that, uncertainty over petroleum reserves and volatile political scenario in Middle East countries, which are the main producers of petroleum in the world also play a role in the soar of petroleum price at global market. On the other hand, utilization of these expensive energy sources is also one of the main causes of environmental pollution. The combustion process of these non-renewable fossil fuels emits excessive toxic gases which include carbon monoxide (CO), carbon dioxide (CO_2), nitrogen oxide (NO), nitrogen dioxide (NO_2) and sulfur dioxide (SO_2) [2–4]. These harmful gases, also known as greenhouse gases (GHGs) are responsible for green house effect phenomenon as they can trap enormous amount of heat in the atmosphere and subsequently causing global warming and acid rain. With the trend of escalating demand in fossil fuels as the main source of energy throughout the world, this problem has become a global issue and the quest for a

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cleaner, environment-friendly and renewable source of energy is inevitable.

For the past two decades, the search for alternative energy which is renewable and environmental-friendly has been carried out extensively over the world. Renewable energy is derived by utilizing inexhaustible natural resources including sunlight, wind, tidal and geothermal heat. Hence, renewable energy sources do not emit excessive harmful gases or particulates to environment compared to non-renewable fossil fuels. Instead, it has the potential to mitigate climate change and solve environmental pollution crisis in the world. For instance, renewable energy such as biodiesel is produced from crops and biomass, which absorb carbon from the atmosphere as they grow. Subsequently, the carbon will be released during combustion process and return to atmosphere. Hence, biodiesel is a carbon neutral source of energy as no additional emission is discharge to the environment during the carbon cycle. Furthermore, biodiesel is superior to diesel in terms of sulfur content, flash point, aromatic content and biodegradability. Apart from being environmental-friendly, liquid biodiesel also offer a promising long term solution for energy security and sustainable development as more than 40% of total energy consumption in the world is in liquid form while other renewable energy sources such as solar, wind and hydrothermal are only able to generate electricity or thermal energy [5]. In addition, no modification in diesel engine is required as biodiesel is compatible with existing engine model and has been commercially blended with diesel as transportation fuel.

Biodiesel is defined as fatty acid alkyl ester and is derived from triglycerides via transesterification reaction with alcohol such as methanol and ethanol [6]. In this reversible reaction, 1 mole of triglycerides will react with 3 moles of alcohol to produce one mole of glycerol and three moles of fatty acids. If methanol is used as the source of alcohol, methyl esters of fatty acids will be formed. On the other hand, if ethanol is used, ethyl esters of fatty acids will be produced. Both of these fatty acids are commonly known as biodiesel. Generally, the sources of triglycerides are obtained from oil-bearing crops such as rapeseed, soybean and palm. Transesterification reaction can proceed with or without the presence of catalyst. However, without any catalysts the reaction proceeds in an extremely slow rate due to the two phase nature of oil and alcohol [6]. Thus, catalysts are normally added to increase the reaction rate and enhance the yield of biodiesel. Transesterification reaction can be catalyzed by both homogeneous and heterogeneous catalysts. In addition, the catalysts can be either acidic or alkaline such as sulfuric acid, hydrochloric acid, sodium hydroxide and potassium hydroxide which are all homogeneous catalysts. In fact, most of the conventional commercial plants producing biodiesel from vegetable oils have been using these homogenous catalysts. On the other hand, heterogeneous catalysts are being extensively developed for transesterification reaction as well. The main advantage of heterogeneous catalyst is the simplified separation process of biodiesel from catalyst which is relatively easier compared to homogeneous reaction as the catalyst and products are in different physical phase.

Recently, there is a new trend in transesterification reaction with the advancement of supercritical fluids (SCF) reaction to produce biodiesel which do not require the presence of any catalysts. In this non-catalytic process, only reactants are added in the reaction mixture and heated to supercritical alcohol conditions to produce biodiesel which makes the process relatively simple and cost-effective. Although SCF reaction seems to be a promising technology which could solve existing problems of catalytic reactions, there has been a lot of debate on the efficiency of SCF reaction in terms of energy utilization and safety issue due to the high pressure and temperature employed in this technology. Hence, there are challenges and issues that need to be addressed before SCF technology can play a major role in biodiesel production. Consequently, this study aims to review recent trend and progress of transesterification reaction involving catalytic and non-catalytic SCF technologies and subsequently highlights the challenges of SCF process in order to be the main reaction route to produce a sustainable source of biodiesel in the future. Finally, some constructive recommendations to overcome the obstacles facing SCF technology will be proposed as well.

2. Transesterification reaction

Transesterification reaction or also known as alcoholysis is the main reaction that occurs during biodiesel production between triglycerides and alcohol to produce fatty acid alkyl esters and glycerol. Fig. 1 shows the overall transesterification reaction between the two main reactants. The objective of transesterification reaction is to reduce the viscosity of vegetable oils to a value similar to conventional diesel. Neat vegetable oils could not be used directly in the diesel engine due to its high viscosity and low volatility. Besides, it will also cause some carbon deposit and injector coking in the diesel engine. Generally, transesterification is an equilibrium reaction between triglycerides (TG) and alcohol (ROH) which consists of three consecutive and reversible reactions where diglycerides (DG) and monoglycerides (MG) are formed as intermediates as shown in Fig. 2. In this reaction, one of the alkoxy groups in the triglycerides is replaced by another alkoxy group in the alcohol to form a new ester compound which is the fatty acid alkyl ester (RCOOR). Finally, after all the three alkoxy groups available in triglycerides have been replaced, three mol of fatty acid alkyl ester and one mole of glycerol molecule will be formed. As these reactions are reversible, a larger amount of alcohol than stoichiometry requirement is usually employed to shift the reaction equilibrium to produce more alky esters.

2.1. Catalytic reactions

Generally, alcohol and vegetable oil are not miscible to form a single phase of solution. Hence, the poor contact area between these two reactants causes transesterification reaction to proceed relatively slow. Consequently, vigorous mixing and stirring are carried out in order to promote and enhance solubility between these reactants and subsequently improve the reaction rates. Apart from that, temperature plays a crucial role in determining the reaction rate of the transesterification reaction. For instance, at ambient temperature, the reaction requires up to 8 h for completion. On the other hand, if the reaction was conducted at 60 °C, a mere 90 min of reaction time will be needed. Hence, introduction of catalysts at elevated temperature will improve the reaction rates and biodiesel yield as it is able to solve the problems of two-phase nature between oil and alcohol.

Homogeneous base catalysts such as sodium hydroxide and potassium hydroxide are commonly and widely used in commercial biodiesel plant throughout the world. These soluble catalysts are inexpensive and effectively enhanced biodiesel production by producing intermediate of methoxide which will react with oil to produce biodiesel and glycerol. However, if the vegetable oil contains a high proportion of free fatty acids (FFA) or water, side formation of soap from FFA and base catalysts will occur which affect the yield of biodiesel substantially. Hence, homogeneous acid catalysts including sulfuric acid, phosphoric acid and hydrochloric acid are more suitable to be employed as no side reaction will occur in oils/fats which contains high percentage of FFA and water.

Homogeneous acidic and alkaline catalysts processes have been proven to be able to produce a significantly high yield of biodiesel from triglycerides and alcohol in a short reaction time. However, these homogeneous reactions have several weaknesses and

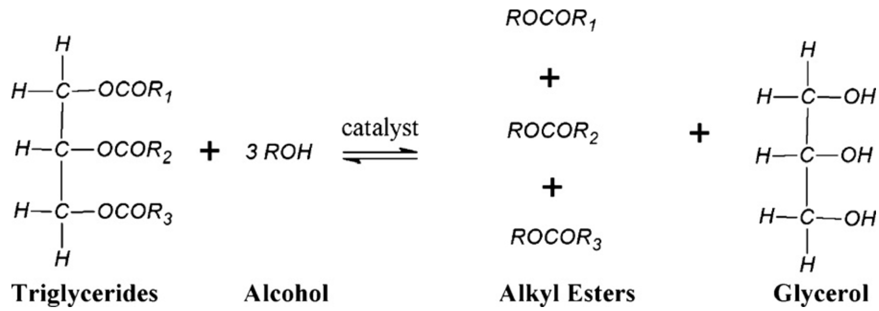

Fig. 1. General transesterification reaction between triglycerides and alcohol.

$$\text{Triglycerides (TG)} + ROH \rightleftharpoons \text{Diglycerides (DG)} + RCOOR_1$$

$$\text{Diglycerides (DG)} + ROH \rightleftharpoons \text{Monoglycerides (MG)} + RCOOR_2$$

$$\text{Monoglycerides (MG)} + ROH \rightleftharpoons \text{Glycerol (GL)} + RCOOR_3$$

Fig. 2. The three reversible and consecutive reactions in transesterification of triglyceride.

drawbacks which make them unattractive in term of economic consideration. For instance, the homogeneous phase of catalyst and products makes separation and purification steps complex and energy-consuming. Moreover, the alkaline and acidic waste water generated from the separation required additional cost for disposal. Apart from that, the recovery of glycerol is difficult due to the solubility of excessive methanol and catalyst. Besides, alkaline-catalyzed reaction is not recommended if high FFA and water content are present in vegetable oils or other triglycerides sources such as tallow, non-edible oils and waste cooking oil.

Recently, there has been a growing interest in heterogeneous catalytic transesterification reaction due to its advantages compared to homogeneous reactions. For instance, problems facing homogeneous catalytic reaction such as tedious separation and purification of biodiesel will not arise as the catalyst and products are in different phase. Furthermore, heterogeneous catalysts can be recovered and reused easily which reduces the cost of catalyst significantly. Besides, it is not affected by the presence of high content of FFA in oils/fats. However, compared to homogeneous reaction, heterogeneous process proceeds at a relatively slower reaction rate due to the three-phase system of oil, alcohol and solid catalyst. In addition, solid catalysts are sensitive to the presence of water in reaction mixture which leads to leaching phenomenon of active compounds in catalysts. Consequently, catalyst efficiency is adversely affected and resulted in lower biodiesel yield [6]. On the other hand, enzymes such as lipase are also extensively employed as well in transesterification reaction to enhance the reaction rate. Immobilized enzymes on a support material were found to be able to produce high purity of biodiesel and allow easy separation of glycerol. Furthermore, immobilized enzymes can be used repeatedly to increase the cost effectiveness of this catalytic process. However, enzymatic reaction suffers from long reaction time and inhibition effect of glycerol on enzymatic activities which makes the process become uneconomical [6].

2.2. Non-catalytic supercritical fluids (SCF) technology

Homogeneous and heterogeneous catalytic reactions have been shown to have several limitations which include sensitivity to high water and FFA content, complicated separation and purification of biodiesel, enormous amount of reaction time and exorbitant cost of catalysts which make the process uneconomical. Collectively, these weaknesses arise due to utilization of catalysts in transesterification reaction. However, without the presence of catalysts, the reaction rate is too slow for it to produce considerable yield of biodiesel. Hence, researchers around the world have been developing numerous alternative technologies which can solve the problems facing catalytic reaction by using non-catalytic processes.

One of them is by applying supercritical alcohol (SCA) technology, which has been getting a lot of attention lately [7,8]. This novel technology utilizes SCA conditions to allow the usually immiscible oil and alcohol to form a single phase of solution. This would solve the problems of limited contact area between these two reactants which causes the reaction to occur at a slow rate. For methanol, the critical temperature and pressure are 239 °C and 8.1 MPa, respectively while for ethanol; it is 243 °C and 6.3 MPa, respectively. Moreover, without the presence of catalyst in the process, the cost of production can be reduced substantially. In SCA reaction, triglycerides and alcohol are heated until the critical temperature and pressure of alcohol is reached and allows transesterification reaction to occur.

During supercritical conditions of alcohol, the solubility parameter of alcohol is reduced substantially to a value near to triglycerides which leads to formation of a homogeneous phase between these two reactants. Hence, transesterification reaction can proceed without the presence of catalyst and the reaction rate for SCA was found to be superior to catalytic reactions as well [9]. In addition, downstream processes to separate biodiesel from glycerol were found to be simple with the absence of catalyst and the glycerol obtained was found to be of high purity. Furthermore, SCA process has a high tolerance towards impurities such as FFA and water in oils/fats and no side reaction of saponification was reported [10]. Instead, in this non-catalytic reaction, transesterification of triglycerides and esterification of FFA occur simultaneously in reaction mixture which leads to higher biodiesel yield. Furthermore, the presence of water will not adversely affect the reaction rate but was found to cause hydrolysis of triglycerides to FFA which subsequently can be esterified to produce fatty acid alkyl esters. Hence, SCA reaction allows the employment of inexpensive feedstock such as waste oils/fats which commonly contained high proportion of these impurities.

Recently, there is an emergence of a new SCF technology which employs methyl acetate as supercritical medium rather than alcohol [11,12]. The application of alcohol in conventional transesterification reaction produces glycerol as side product which leads to oversupply and devaluation in the market value. In addition,

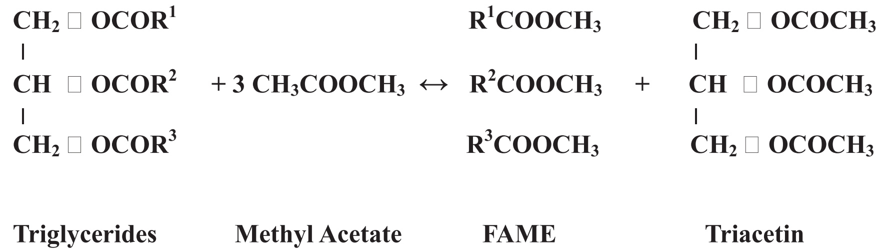

Fig. 3. Reaction stoichiometry for transesterification reaction between triglycerides and methyl acetate.

biodiesel shows inferior performance at low temperature due to high viscosity and cloud point which limits its commercial application at cold climate countries. Therefore, biodiesel additive is commonly added into biodiesel to enhance its performance during cold season. On the other hand, in Supercritical Methyl Acetate (SCMA) reaction, Fatty Acid Methyl Esters (FAME) and triacetin, instead of glycerol are produced as shown in Fig. 3. Triacetin, a valuable fuel additive is formed simultaneously which leads to simplified downstream processes compared to conventional catalytic reactions while the mixture of FAME and triacetin can be utilized as biodiesel, rather than FAME only. In this context, the mass ratio of FAME to triacetin was found to be approximately 4:1 in weight percent basis. Consequently, the total theoretical weight of biodiesel (FAME and triacetin) was found to be 125%, instead of 100% (FAME only). Hence, SCMA reaction is a promising technology for biodiesel production which not only can improve the quality of biodiesel but also minimizes the cost of producing biodiesel additives. Apart from that, in this glycerol-free process, separation and purification processes are simpler and less energy-intensive since both products could be utilized as biodiesel mixture.

Apart from SCMA reaction, there is another alcohol-free supercritical reaction which has been researched extensively. Similar to SCMA reaction, Supercritical Dimethyl Carbonate (SCDMC) also does not produce glycerol as side product but instead of triacetin, a valuable compound of glycerol carbonate (GC) is formed [13,14]. GC is a glycerol derivative which has enormous applications in polymer and membrane industries and most importantly has higher market value than crude glycerol. Conventionally, GC is produced by revalorizing glycerol obtained from transesterification reaction by phosgenation method or direct carboxylation. However, these methods suffer from either toxicity limitations or low yield of GC which leads to uneconomical production. Consequently, it is vital to search for an alternative process which could produce GC and biodiesel in a more economical process to address issues of glycerol glut and elevated cost of biodiesel. Hence, production of biodiesel via SCDMC process will make total production costs to be more profitable as biodiesel and the valuable GC could be produced simultaneously in this single-step reaction, instead of the conventional two-step reactions involving transesterification with methanol and subsequently glycerol revalorization with dimethyl carbonate. This innovative and cost-effective process of SCDMC will be able to help biodiesel producer to generate side income and subsequently leads to cost-effective biodiesel route.

3. Challenges and limitations of SCF technology

Although SCF technologies have enormous advantages compared to conventional catalytic reactions as discussed previously, there are several challenges and weaknesses that need to be addressed before SCF could play a major role in biodiesel production. Hence, in this section the limitations of SCF process will be highlighted and discuss thoroughly and subsequently recommendations to overcome these challenges will be proposed in the next section.

3.1. Energy consumption

One of the weaknesses of SCF technology is the apparent high energy required to reach the supercritical conditions of the solvent. The high temperature and pressure needed in the process, depending on the type of solvents employed, consume a huge amount of energy which is unsustainable in the long term. For instance, in SCM reaction, the temperature and pressure must be above 239 °C and 8.1 MPa, respectively in order to achieve supercritical methanol state which makes SCF technologies an energy-intensive process. Comparatively, it is widely reported that conventional catalytic reactions only require average reaction temperature <150 °C and atmospheric pressure for optimum biodiesel production [15]. In addition, there are also concerns that the energy utilized in the process is more than the energy provided by biofuels obtained from SCF technology. In other words, more energy is required to yield products (biofuels) which have less energy content. Consequently, it is claimed that SCF technology is unsustainable in terms of energy consumption and subsequently not suitable for biodiesel production.

3.2. Cost

Apart from energy consumption, one of the major obstacles in commercialization efforts of SCF technology is the huge cost involved in the process. For instance, the elevated temperature and pressure needed in supercritical conditions required huge amount of energy which involved expensive expenditure in high pressure pumps and furnaces. Furthermore, employment of SCF technology to produce biodiesel requires high amount of solvent to push the reversible reaction to produce more biodiesel. Consequently, the high cost of reactant as well as additional processes to recover unreacted solvent increases the total expenditure in SCF reaction. In addition, due to the nature of SCF reaction conditions, the material of construction for most reactors in SCF technology are usually fabricated with additional strength and durability in order to sustain the extreme conditions. On top of that, the cost to fabricate a unique and huge reactor for commercialization purposes will be enormous. Hence, the costs involved in operation and maintenance of SCF process is relatively higher compared to conventional catalytic reactions. Consequently, there has been limited commercialization projects of supercritical-based biodiesel production due to the huge amount of costs involved in materials, operation and maintenance.

3.3. Safety issue

In SCF process, the extreme conditions of high temperature and pressure have lead to debate over safety issue of the operation. For instance, in supercritical methanol reaction, the reaction pressure is higher than 8.1 MPa, which is adequate to cause catastrophe effect if there were any leakages on the reactor vessel. This possible hazardous scenario has lead to concern regarding safety of supercritical reaction plants which has abstain most investors from

investing in this technology. Hence, supercritical-based reactions have been labelled as high risk process and insecure to be employed in biodiesel production.

4. Recommendations

The potential and advantages of SCF process to produce biodiesel is enormous compared to conventional catalytic reactions in terms of rapid reaction rate, high yield and simplicity in downstream processes. However, as discussed earlier, SCF technology also has limitations and challenges which need to be addressed and solved before it is suitable to be employed commercially in biodiesel production. Hence, in this section, recommendations to address these issues will be discussed and elaborated thoroughly which is vital to improve SCF process and subsequently play a major role in biodiesel production.

4.1. Integrated heating and cooling system

Supercritical reaction requires huge amount of energy to carry out the reaction at elevated temperature and pressure and subsequently cool down to room temperature when the reaction is complete. The enormous energy to provide heat to the reactor and cooling effect upon reaction completion leads to claims that SCF is an energy-intensive process. Hence, it is vital to modify and improve SCF process which will minimize the amount of heat involved in heating and cooling procedures. One of the methods is to install a double tube heat exchanger before the supercritical reactor to allow pre-heating of fresh reactants by stream exiting the reactor. In this context, the integrated heat recovery system would reduce the heat duty substantially as the heating of reactants and cooling of products are carried out by a heat exchanger, instead of two independent heating and cooling mechanisms. Hence, the total energy required in SCF reaction could be diminished significantly which is vital for commercialization purposes. Recent studies have concluded that the total energy required for SCA and conventional catalytic reactions are relatively similar when integrated heating and cooling system is employed in SCA reaction [16–18]. This finding validates that SCF technology is not an energy-demanding process but instead requires comparable energy consumption to other existing processes.

4.2. Two-stage reaction

As discussed previously, the high cost of huge SCF reactor and high molar ratio of reactants needed makes the process unattractive from economic point of view. However, these limitations can be overcome by employing two-stage supercritical reaction, instead of conventional single-step reaction. It was reported that two-stage SFC reaction involves lower pumping power and heat duty as the size of the reactor is reduced substantially compared to single-reactor reaction [16]. On top of that, two small size reactors in series will minimize the construction cost of reactor as well as risk associated with operation and maintenance. Hence, the issues of reactor cost and safety could be addressed by employing this system. In addition, the cost of reactants can be decreased as well since the two-stage reaction only require moderate reactant molar ratio which leads to lower reaction pressure.

5. Conclusion

The advantages of SCF technology in biodiesel production compared to conventional catalytic reactions are enormous and vital in solving issue of energy security in the future. However, there are several challenges which need to be addressed before SCF technology could play a major role as the main route for renewable and sustainable biodiesel production. Hence, several recommendations were discussed in this article which could improve SCF process in terms of energy consumption as well as costs of material and equipment.

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